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Molecular self-diffusion and micellar structure in the aqueous solutions of AF9-10 ethoxylated isononylphenol near a cloud point

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Sizes of micelles and compositions of aggregates in the aqueous solutions of the nonionic surfactant oxyethylated monoalkyl phenol (neonol AF9-10) were determined by NMR spectroscopy, NMR diffusometry and dynamic light scattering in a wide range of temperatures near the cloud point. The cloud point extraction of phenol from aqueous solutions by the surfactant AF9-10 was performed.

In the aqueous solutions of nonionic surfactants, turbidity is observed with increasing temperature due to a phase transition from uniform micelles to nonuniform biphasic solution consisting of a surfactant-depleted phase and a surfactant-rich phase.[1] The turbidity or cloud of the solution results from light scattering by density fluctuations formed by irregular surfactant aggregates, whose dimensions are comparable to wavelengths in the visible range.

An increase in surfactant concentrations leads to a change in the micelle shape from spherical to rod-like. The core of micelles is formed by hydrophobic hydrocarbon tails, while hydrophilic polar oxyethylene chains form a thick extensive surface of micelles. The micelles contain water associated with oxygen of surfactant oxyethylene groups through hydrogen bonds. The cloud phenomenon is explained by the dehydration of oxyethylene chains under increasing temperature and by the formation of aggregates (clusters) of dehydrated surfactant molecules, which have low solubility in water and are prone to sedimentation. Changes in the surfactant properties with cloud point (CP) transition are used in a cloud point extraction (CPE) method, which is applied to extract hydrophobic organic compounds such as phenols and polycyclic aromatic hydrocarbons.[2,3] The aim of this work was to study the properties of nonionic surfactants near the CP using aqueous solutions of oxyethylated monoalkyl phenol (neonol AF9-10). Neonol AF9-10 is a water-soluble high-effective nonionic surfactant. The CP of an aqueous solution of AF9-10 with concentration 10 g dm^{-3} is 66±3 °C. We used NMR diffusometry, NMR spectroscopy and dynamic light scattering at a constant AF9-10 concentration of 10 g dm^{-3} in a temperature range of 30–90 °C. This temperature range covers the region of existence of micellar solution, the transition region near the CP and the region of two-phase solution containing aggregates of surfactant molecules. Removal of phenol from aqueous solutions by the CPE method using AF9-10 was analyzed.[†]

Neonol solutions were transparent below the cloud point, while they were bluish-white above it. Therefore, it is believed that micelle sizes below the CP did not exceed 50 nm, and aggregates or clusters formed above the CP had dimensions of 100–1000 nm.

In the study of fast processes or thermal studies, one should take into account the rate of relaxation processes of nuclear magnetization, the spin–spin and spin–lattice relaxation. We measured the integrated intensities of the protons of water and surfactant oxyethylene groups in ^{1}H NMR spectra[‡] to understand what changes occur in micelle composition near the cloud point. To minimize the error of integration of closely spaced lines, two kinds of solutions were prepared: in ordinary water H_2O and in deuterated water D_2O, and accordingly, two series of measurements were carried out. In the H_2O solutions, the integrated intensities of water lines were measured, while the contributions of oxyethylene protons could be neglected because of a low surfactant concentration. In the D_2O solutions, we measured the integrated intensity of surfactant oxyethylene protons; in this case, the contribution of deuterated water residual protons was negligible.

To avoid distortion of the integrated intensities in the NMR spectra due to a saturation phenomenon, rest time was chosen $\approx 5T_1$ (T_1 is the spin–lattice relaxation time). Relaxation times T_1 measured by the two-pulse sequence 180°–τ–90° with increasing temperature from 30 to 90 °C ranged within 1.9–2.8 and 5–20 s for water protons and residual protons of deuterated water, respectively. The relaxation times of oxyethylene protons in all solutions did not exceed 1 s. The integrated intensities were compared with each other considering the temperature dependence of the magnetic susceptibility (Curie law) and water density.

Selective measurements of self-diffusion coefficients (SDCs) of water and surfactant molecules were carried out by an NMR spin echo technique with a pulsed magnetic field gradient.[‡,4] The maximum amplitude of a pulsed magnetic field gradient was 0.5 T m^{-1}. The Fourier transformation of the echo signal allowed us to obtain in one experiment the SDCs of different molecules characterized by distinct NMR chemical shifts.[5,6] We experimenally estimated surfactant SDCs using diffusion decays of the signal of oxyethylene protons (4.0 ppm), while SDCs of water molecules were determined from diffusion decay

[†] Commercial AF9-10 [$C_9H_{19}C_6H_4O(C_2H_4O)_{10}H$] from Nizhnekamskneftekhim (Russia, www.elarum.ru/standarts/tu-2483-077-05766801-98) was used without further purification. Chemically pure phenol (Sigma), deionized water and deuterated water (99%, Sigma) were used to prepare solutions.

[‡] The NMR spectra were recorded using Tesla-BS567A (^{1}H, 100 MHz) and Bruker Avance 400 WB (^{1}H, 400 MHz) spectrometers. The measurements of SDCs were performed using a Tesla-BS567A spectrometer equipped with a pulsed gradient unit.